Senior Honors Thesis

Strontium Isotopes in Redmond Creek Cave, Monticello, Kentucky

by
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Dr. Kenneth A. Foland

Abstract

Redmond Creek Cave is located near Monticello in Wayne County of south-central Kentucky, as shown on Plate 1. The cave cuts through the Kidder and Ste. Genevieve limestones and is overlain by the Hartselle, Bangor Limestone, Pennington, Breachitt, and Lee Formations.

Strontium isotopes have been used to evaluate the sources of Sr in groundwater and to see if they changed over time. The $^{87}Sr/^{86}Sr$ ratios and Sr concentrations have been analyzed in bedrock and water samples taken from the surface, the cave, and its main insurgence and resurgence. Water from both the dry and wet seasons were analyzed. Also, different growth layers of a stalactite were analyzed to evaluate long-term variations.

Significant variations are observed with $^{87}Sr/^{86}Sr$ ranging from 0.7082 to 0.7078 for limestone bedrock and from 0.71307 to 0.70837 for water. Sandstones of the Hartselle and Lee Formations have the highest $^{87}Sr/^{86}Sr$ ratios, up to 0.7337. In contrast, limestones of the Kidder and Ste. Genevieve formations have the lowest $^{87}Sr/^{86}Sr$ ratios near 0.7080; the limestone values are consistent with the seawater $^{87}Sr/^{86}Sr$ during the Mississippi when these rocks formed. All water samples are intermediate, indicating that they have mixed sources of their Sr. Some changes in these over time are apparent. Water from dripping speleothems have ratios closer to the limestone. The $^{87}Sr/^{86}Sr$ ratios in a stalactite show only minor variations. Overall, the values of $^{87}Sr/^{86}Sr$ in water and formation appear to reflect the paths of water flow and the degree to which the water interacted with bedrock of various types.

Acknowledgments

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The program, Compass, was used to plot the cave map.

Table of Contents

List of Tables page

List of Figures page

List of Plates

I. Introduction

Strontium isotopes were studied in materials from the Redmond Creek Cave system in south central Kentucky. The location is shown in Plate 1. This was done to investigate the sources for waters that may have formed the cave and precipitated the calcite and gypsum speleothems. Strontium isotopes were analyzed in samples of bedrock, waters, and layers of a stalactite.

II. Background

Cave Formation

Limestone caves form by the dissolution of limestone bedrock by groundwater containing carbonic acid. As rainwater passes through the atmosphere and soil, carbonic acid forms by the reaction:

$$H_2O + CO_2 = H_2CO_3$$

A small fraction of this weak acid dissociates to produce hydrogen ions and bicarbonate ions, i.e. :

$$H_2CO_3 = H^+ + HCO_3^-$$

The carbonic acid then dissolves the limestone bedrock that it passes through where the overall reaction is:

$$CaCO_3 + H_2CO_3 = Ca^{+2} + 2(HCO_3^-)$$

When a cave first starts forming, the water is moving slowly, generally less than 10 meters pear year, through joints, partings, or faults (Moore, 1964). Dissolution is slow initially because the acidity required for dissolution is quickly consumed by calcite dissolution. However, it may be increased in areas by acids produced by the oxidation of sulfides in the limestone. As the channel gets larger, dissolution increases. The critical channel size for this increase in growth is a diameter of 5 millimeters.

The next stage in development is the formation of master channels. These master channels form under phreatic conditions. Three factors are present at the water table that makes formation of master channels possible. These are:

1. The CO_2 content in this zone is high.
2. This water is in contact with limestone long enough to dissolve a significant quantity of limestone.
3. The mixing of groundwater and downward-percolating waters with different CO_2 contents leads to an undersaturated mixture with excess CO_2 which is capable of dissolving more limestone.

Finally, there is a transitional stage where the seasonal effect of nearby streams affect the water level inside the cave. River silt can be introduced at this time (Moore, 1964).

Domepits are cracks or joints that have been enlarged by dissolution by fast-moving water moving vertically. They have vertical grooves and are generally found under the head of a stream valley, beneath the center of a sinkhole, or along a line where a layer of impermeable non-carbonate rock has been eroded off of limestone.

The lowering of the water table and introduction of air passages stops the process of cave formation. The introduction of air passages into the system prevents the maintenance of the high partial pressures of CO_2 (Moore, 1964). After this happens, surface streams and ground water may enter the cave and sculpt scallops on the cave walls.

Speleothems

A speleothem is defined as "a secondary mineral deposit formed in caves" by Hill and Forti (1997). Speleothems form as carbonate or other mineral precipitate from saturated waters in air-filled cavities by various mechanisms. The dominant mechanism of carbonate precipitation in limestone caves is carbon dioxide exchange. The carbon dioxide content of well-ventilated cave is generally 10 times higher than that of surface air and 25 to 250 times lower than the groundwater content (Hill and Forti, 1997). The groundwater loses its carbon dioxide when it hits the air until equilibrium is reached. These reactions are:

$$CO_2(aq) = CO_2(gas)$$

$$H_2CO_3(aq) = H_2O + CO_2(aq)$$

$$Ca^{+2} + 2(HCO_3^-) = CaCO_3 + H_2CO_3$$

Evaporation of incoming groundwater can also cause supersaturation and deposition. High humidity common in caves may make evaporation less of a factor. A common-ion effect is most important in gypsum caves where H_2CO_3 dissolves gypsum. This solution rapidly reaches saturation of $CaCO_3$ and calcite is deposited (Hill and Forti, 1997).

Speleothems are classified primarily by morphology, then by origin and composition. Samples were collected from the various speleothems described here. Stalactites have the same morphology as an icicle. They begin as soda straws (a thin-walled, hollow formation about three millimeters in diameter) that form as calcite crystals form around the edges of saturated drops of water on the ceiling. This soda straw forms the central canal of the stalactite. Simultaneously, the outside layers form as crystals build perpendicularly to the walls of the soda straw as water flows down the outer surface of the speleothem (Hill and Forti, 1997). A stalactite is shown in Figure 1.

Rimstone dams have a stair-step morphology. They build up as barriers perpendicular to flow that obstruct cave streams or pools. They form as crystallization occurs at the water/ice/rock interface and often grade into flowstone with gradient changes (Hill and Forti, 1997). Rimstone dams are shown in Figure 1.

Flowstone is a sheet-like deposit that has a crystal orientation that builds up perpendicular to flow. In Redmond Creek Cave the flowstone is mostly canopy flowstone that projects laterally away from the walls and formations.

Gypsum flowers consist of both fibrous and prismatic crystals growing in approximately parallel orientation. Curving found in these formations is caused by changes in flow rate of supply solution, change in the concentration of these solutions, or interruption in the supply solution. Gypsum also forms crusts on the ceilings and walls of some rooms and passages in Redmond Creek Cave. A gypsum flower is shown in Figure 2.

Karst hydrology and water geochemistry

Karst aquifers are described as conduit-flow or diffuse flow. In a diffuse-flow aquifer, groundwater movement takes place through primary permeability and fracture permeability. Conduit-flow aquifers have a well-developed conduit permeability. The primary porosity of the Ste. Genevieve Limestone is 3.3% and its coefficient of permeability is 0.0016 liter/day/m^2 (Choquette and Steinen, 1980)

The mean number of annual series of floods for basins in thick carbonate is low compared to basins underlain by clastic rocks. This is due to flood water storage in the aquifer with slow resurgence over time. Sinking streams in karst environments often obtain an overbank stage while flood waters are being stored (Hess et al., 1989).

Karst waters have varying levels of carbonate saturation. Both saturated and undersaturated waters occur in the vadose zone. Vertical shaft waters are among the most undersaturated waters. Seepage waters are the only supersaturated waters in the system. Water that discharges from springs is undersaturated. Variations in concentrations are controlled on an annual cycle by the rate of CO_2 generation and its seasonal variation (Hess and White, 1989).

Regional Geology

Redmond Creek is on the southeastern limb of the Cincinnati arch. The Cincinnati arch is a broad anticlinal structure that extends from the Lexington Dome in the north to the Nashville dome in the south (Hess et al. 1989). This is at the junction of the Mississippi plateau and the Cumberland Plateau in south-central Kentucky. The overlying Pennsylvanian rocks are part of the Cumberland Plateau. The underlying Mississippian rocks are part of the Mississippi Plateau. In most areas of Kentucky, this boundary is disconformity, but in this area, there is continuous deposition from the late Mississippian to the early Pennsylvanian. The Mississippian rocks here are principally marine in origin. They conformably overlie late Devonian rocks, which are mostly dark carbonaceous shale. A Pennsylvanian fossil, lepidodendron, has been found in dry surface streams over Redmond Creek Cave. A geologic map (from the Pall Mall Quadrangle, 1977) is shown as Plate 2. A geologic cross section of the cave is shown in Plate 3.

The Mississippian rocks in Kentucky consist of four major groups (Rice, 1979). These are:

1. Distal terrigenous detrital deposits made up of shale, siltstone, and sandstone that are from westward and southward prograding deltaic systems (Rice, 1979). These rocks are not seen in this area.

2. Marine carbonate deposits made up of limestone and dolostone that are partially basinal but mostly shallow-water shelf deposits. This group includes the Ste. Genevieve Limestone (Rice, 1979).

The Ste. Genevieve Limestone is 60 to 130 feet thick. It is composed of limestone that is partially oolitic. Beds are 3 to 10 feet thick and are mostly crossbedded. Chert beds are also present. The limestone contains some brachiopods and horn corals (Lewis, 1977).

3. Rhythmically alternating marine carbonate and terrigenous detrital deposits. The shallow-water shelf limestones alternate with sandstone and shale from a southward and southwestward prograding delta (Rice, 1979). This includes the Kidder Limestone, the Bangor Limestone, and the Hartselle Formation, which are all in the area of the cave.

The Kidder Limestone is 110 to 140 feet thick and is composed of limestone, minor shale, and siltstone. The limestone is partly oolitic, thin to thick bedded, partially cross-bedded, has some thin interbeds of calcareous shales and siltstones, and contains abundant fragments of brachiopods, blastoids, and crinoids (Lewis, 1977).

The Hartselle Formation ranges from 8 to 40 feet thick. It is composed of sandstone and shale. The sandstone is fine to medium grained, thin to thick bedded, has lingulate ripple marks on bedding surfaces. (These were observed at the contact at the main insurgence.) It is composed of angular to subangular quartz grains, minor mica grains, and dark rock fragments (Lewis, 1977).

The Bangor Limestone ranges from 35 to 65 feet thick. It is composed of limestone that is medium too thick bedded, partially crossbedded, and, in part, is cherty. It is composed of fragments of bryozoans, brachiopods, blastoids, and crinoid stems in a sparry calcite matrix (Lewis, 1977).

4. Terrigenous detrital deposits including shales, sandstones, and some limestones and dolostones of westward and southwestward prograding deltaic systems. This includes the Pennington Formation, and the Breathitt and Lee Formations which cap the hill that overlies Redmond Creek Cave (Rice, 1979).

The Pennington Formation ranges from 70 to 220 feet thick and is composed of shale, limestone, siltstone, and sandstone. Beds are 6 inches to 4 feet thick. The limestone is partially oolitic, crossbedded, dolomitic in places, and fossiliferrous in part with abundant fragments of crinoids, blastoids, bryozoans, and spiriproid brachiopods. The limestone is common in the lower sixty feet of the formation. The siltstone is interbedded with shale in the middle and upper parts of the formation. The sandstone is fine to medium grained, quartzose, micaceous, and thin to thick bedded (Lewis, 1977).

The Breathitt Formation is 380 or more feet thick and is composed of shale, sandstone, and coal. The shale in the lower part of the Formation is interbedded with thin lenses of sandstone. It contains plant fragments and thin lenses of coal. The sandstone is quartzose, fine to medium grained, subangular to well-rounded, well-sorted, crossbedded, and occurs as lenses and channel fill that is up to 30 feet thick. The coal is mostly bituminous and contains some thin stringers of pyrite (Lewis, 1977).

The Rockcastle Sandstone Member of the Lee Formation ranges from 0 to 120 feet thick and is composed of sandstone and conglomerate. The sandstone is quartzose, medium to coarse grained, medium to thick bedded, and commonly crossbedded. The conglomerate is composed of well-rounded quartz pebbles in a silica-cemented sand matrix, and is found in irregular pods and lenses in the lower fifteen to twenty feet of the member (Lewis, 1977).

Sr isotopes

Strontium is used here as a tracer to find source for groundwater in the cave and to find the provenance for limestone. Strontium is a member of the alkaline earths of group IIA. It substitutes for calcium and magnesium in many minerals, especially aragonite, calcite, and gypsum. Strontium has four naturally occurring stable isotopes: ^{88}Sr, ^{87}Sr, ^{86}Sr, and ^{84}Sr. Three of the four isotopes occur in the same proportion. The other, ^{87}Sr, has variable abundance. This is because ^{87}Rb decays by beta emission to ^{87}Sr (with a half-life of 48.8 billion years). Because of variations in radiogenic ^{87}Sr, the ratio of $^{87}Sr/^{86}Sr$ may serve as a powerful tracer (see further discussion in Faure, 1986; Dickin, 1995).

Different crustal rocks have different $^{87}Sr/^{86}Sr$ ratios and ages. Rocks with high Rb/Sr will be expected to have more radiogenic Sr (i.e. high $^{87}Sr/^{86}Sr$). The average crustal ratio is about 0.720. Clastic sediments are likely to have high ratios depending on their sources. Also, clastic sedimentary rocks themselves will have more Rb and thus may develop elevated $^{87}Sr/^{86}Sr$ over geologic time. Limestone averages about 610 ppm Sr and 3 ppm Rb while sandstones have about 60 ppm Rb and 20 ppm Sr (Faure, 1986). Marine seawater is expected to have a value similar to the seawater from which they form. The $^{87}Sr/^{86}Sr$ value for seawater has varied over time but is less than then those values for the average continental crust and most crustal rocks.

As a result, it is expected that the clastic bedrock of the Redmond Creek area have a higher $^{87}Sr/^{86}Sr$ ratio than the carbonates. Water that interacts with or gains Sr from the bedrock will have Sr ratios reflecting the type of rock. Therefore, the $^{87}Sr/^{86}Sr$ has the potential to serve to identify the sources of Sr and, thus, the bedrock from which it was acquired.

Redmond Creek Cave

Redmond Creek Cave is in Wayne County, Kentucky, south of the town of Monticello. A map of the cave is shown in Plate 4. The entrance of Redmond Creek Cave is in the Ste. Genevieve Limestone. It is an outflow entrance that feeds Redmond Creek on the surface, which flows into Otter Creek. This entrance and the streambed downstream of the entrance are dry most of the year. Redmond Creek flows with water downstream where many streams including the main resurgence of the cave feed it.

The main stream passage, into which the entrance drops, trends north-south with the water flowing mostly to the north. This passage is about 15 to 30 feet wide and ranges from 4 to 20 feet high. The bottom of the passage is covered with subrounded quartz grains, ranging from sand-sized to cobbles, that are a several centimeters in diameter. This passage continues in the Ste. Genevieve Limestone, dipping with the bedrock at a four-degree angle, until the lowest point in the cave. Water pools at this point in the cave, which is about 1500 feet into the cave. After this, the passage trends up into the Kidder Limestone.

The contact between the Kidder and Ste. Genevieve Limestones is a limestone breccia bed that has not been located in the cave. It is thought to be found in some breakdown just south of the lowest point in the cave. The main stream passage continues through the Kidder Limestone with the same dimensions. It connects with canyon passages going east and west that connect with upper level passages continuing in those directions. Just beyond the connection with the west canyon passages, the height of the main stream passage reduces to a few inches.

Gypsum coatings and formations characterize the upper level passages west of the main stream passage. This is also found in the Mammoth Cave region where the gypsum in upper level passages is supplied by vertical seepage that moves beneath the caprock. Humidity in these passages in the Mammoth Cave system is relatively low; it can go as low as 80% (Hess et. al., 1989).

Lots of quartz rocks are found in the east canyons. About eighteen very-well rounded quartz egg-shaped rocks are found in the pool of a dome pit in an eastern canyon. These "eggs" are softer than pure quartz and may be quartz that has come out of solution in the cave.

Redmond Creek Cave has many silicified crinoid, echinoderm, and corral fossils. These fossils are common in the Ste. Genevieve and the Kidder Limestones. The cave frequently floods to the ceiling in the late winter or the early spring. Life in the cave includes solitary bats which are *Pipistrellus subflavus* and *Myotis lucifungus* (MacGregor, 1985), cave crayfish which are *Orconectes (Orconectes) australis packardi* (Horton H. Hobbs III, oral communication to Bill Walden, May 1999), cave crickets, and cave beetles.

III. **Methods**

Sample collection

The author has been surveying Redmond Creek Cave with the Central Ohio Grotto (an organization for the exploration and conservation of caves) since 1996. Sample collection for this project started on September 5, 1998. Sample collection started in the west section of the cave and continued towards the entrance. Rock samples were obtained from various projections on walls cleaved by a rock hammer. Water samples were collected from undisturbed waters using polyethene bottles. This day was during the cave's dry season. Water levels were relatively low.

More samples were collected on November 27, 1998, when a stalactite sample was obtained. Water levels were higher on this trip than they had been in September. There were clean white formations next to dark red formations in the room where the stalactite was collected. A water sample, kw2, was collected beneath the stalactite before the stalactite was removed. Water was also obtained from a large stalactite between the two entrances this day. On the next day, water samples were obtained from the surface. The water sample, kw3, was obtained from a sinking sidestream off of Redmond Creek. Water was also obtained from the main resurgence of the cave. This spring flows throughout the year. Local people get their drinking water from this spring.

The last group of samples was collected on March 20, 1999. Rock and water samples were collected from inside of the cave. Water levels were a few feet higher on this day than they had been in November. Water samples were collected from the same locations as before to see if strontium ratios varied between the wet and dry seasons. It did rain some the night of March 20. On March 21, 1999, rock and water samples were collected from the surface. Previous surface water sample locations were repeated as much as possible. The sidestream location of sample kr3 was dry this day so a sample was taken from the main insurgence instead. The cave was again visited on May 1, 1999. On this day, the cave was flooded to the ceiling just past the location of water sample, kwE.

When the water samples were returned to the lab, they were acidified by the addition of hydrochloric acid. Rock samples were cut and thin sections obtained. A complete list of the samples analyzed in this study is given in Table 1. Brief petrographic descriptions of rock thin sections are given in Table 2. Sample identification uses “kw” for water samples, “kr” for rock samples, and “g” for stalactite samples.

Analyses

A small amount of ^{84}Sr spike solution was added to a teflon dissolution beaker by weight before water and rock samples were added. The rock samples were crushed and about ten milligrams of each sample was weighed out into the beaker. About ten grams of each water sample was weighed out into a teflon beaker. Then the carbonate samples were dissolved in 2N hydrochloric acid. The sandstone and coral samples were dissolved in a mixture of hydrofluoric, nitric, and hydrochloric acids. The acids used were ultra high-purity acids, prepared by sub-boiling distillation. Then each sample was put on a hotplate to digest and/or evaporate to dryness.

The stalactite samples were obtained using a diamond dremmel bit. A drop of ultra-clean water was put on the stalactite at the position where a sample would be taken. A small cavity was then drilled in the stalactite at this location. The drop of water, which now also contained powdered stalactite from the drilled hole, was put into a teflon beaker using a pipette. This material was spiked with ^{84}Sr and dissolved in 2N hydrochloric acid.

After the samples had digested and then dried, they were each redissolved in one milliliter of 2N hydrochloric acid. They were then centrifuged for about seven minutes to remove any particulate material. No visible solids came out of the water samples. The samples were then loaded onto cation exchange columns to separate the Sr by ion-exchange chromotography. 2N hydrochloric acid was used as an elutent. A second pass through the columns then purified the strontium fractions. After being run through the columns, the samples were dried on a hotplate.

Isotopic measurements were made on a Finnigan/MAT 261 fully automated, variable collector mass spectrometer. The samples were dissolved in hydrochloric acid before loading them onto a rhenium double filament. The samples were run multiple times both with and without an activator, Ta_2O_5. The results were very similar in both cases. About 500 nanograms of strontium were loaded when the samples were loaded without the activator. 50 nanograms or less was loaded when the activator was used.

The basic procedures and mass spectrometry used for Sr in the Radiogenic Isotopes Laboratory is detailed in Foland and Allen (1991). The laboratory value for $^{87}Sr/^{86}Sr$ of the SRM 987 interlaboratory Sr standard is 0.710242 ± 0.000010 (one sigma external reproducibility). The Sr concentrations have an uncertainty of $\pm$ 0.1% for the sample aliquot. The $^{86}Sr/^{87}Sr$ are all normalized assuming normal Sr with $^{86}Sr/^{88}Sr$ = 0.119400. Where given, the uncertainties refer to the last digit(s) and are two standard deviations of the mean in-run uncertainties. Reference value of $^{86}Sr/^{88}Sr$ for the SRM987 is 0.710242 ± 0.000010 (one-sigma external reproducibility).

Table 1: Samples analyzed and descriptions of their sampling locations.

Sample Name	date that sample was obtained	Location & Description
krss	1-2-99	This sandstone sample was taken from the cap of the hill that Redmond Creek Cave goes beneath.
kwA	3-21-99	The main insurgence of the cave is found in the Hartselle Sandstone. Figure 3
kw3	11-27-98	This is a side insurgence in a side stream off of Redmond Creek and this location is in the Kidder Limestone.
krD	3-21-99	This is a limestone sample from the cliff where the main insurgence of Redmond Creek sinks.
krE	3-21-99	This limestone sample was taken from about 20 feet north of krD.
krF1& krF2	3-21-99	This bedrock sample is a fissile sandstone that is interbedded with the cliff at the main insurgence. The fissile sandstone shows ripples and scour marks and is interbedded with the limestone.
g	11-27-98	This sample is a stalactite obtained from an upper-level canyon in the western part of the cave. Calcite from the stalactite's different layers was analyzed.
kr6	11-27-98	This rock sample is a dolostone from a passage beneath the formation.
kw2	11-27-98	This is a water sample that is of water that was dripping down from the formation.
krC1& krC2	3-20-99	This limestone sample was taken from the wall of breakdown room. This room has a coating of gypsum pealing down from the ceiling.
krA	3-20-99	This limestone sample was taken from the 1.5 feet below the ceiling of a canyon passage trending west and curving to the north.
krB	3-20-99	This oolitic limestone sample was taken from about 10 feet up on the canyon wall, about 20 feet below krA.
kw7	9-6-98	This water sample is from a waterfall in a domepit at the end of a canyon trending northwest. The waterfall was trickling.
kwJ	3-20-99	This sample was taken in the same location but in a wetter season for the cave. The waterfall was gushing this day.

Sample Name	date that sample was obtained	Location & Description
kr1	9-5-98	This limestone sample was a taken from a canyon passage leading up into the western section of the cave. The limestone in this area is coated with gypsum, including the sample.
kw8	9-5-98	This water sample was taken from the main stream in the main stream passage at the east passage intersection. Crayfish were in the water here. The stream was flowing slowly to the north, towards the entrance.
kr3	9-5-98	This limestone sample was taken from the main stream passage just above kw8.
kr4	9-5-98	This rock sample is a silicified, colonial rugose coral taken from the ceiling of the main stream passage 100 feet downstream from the east passage intersection. The coral was loosely hanging from the limestone.
kw5	9-5-98	This water sample was taken from water flowing over stalactites, flowstone and popcorn on a wall in the main stream passage. Beneath this stalagmites and rimstone dams. This is 120 feet downstream of the east passage intersection.
kwH	3-20-99	This sample was taken in the same location but in a wetter season for the cave.
kw6	9-5-98	This water sample was taken from water dripping off of a large stalactite in the main stream passage. The stalactite is about 8 feet high and 4.5 feet wide. Rimstone dams are beneath it. This was taken in the cave's dry season.
kwD	3-20-99	This sample was taken in the same location but in a wetter season for the cave.
kwE	3-20-99	This water sample was obtained from the main stream. It was taken at the base of a small domepit. This location was dry in the cave's dry season. The water taken from here was flowing into the cave at this point. The limestone here is banded with black bands of organic material.
kr5	9-5-98	This was a limestone sample taken from inside of the cave. This limestone had dark bands of organic material running through it. Figure 4
kw1	11-30-98	This sample was of water flowing down a stalactite between the cave's two entrances. This sample was taken in the cave's dry season. Figure 1
kwL	3-20-99	This sample was taken in the same location but in a wetter season for the cave. Figure 1
kw4	11-27-98	This resurgence of the cave is a spring that feeds a creek about two miles downstream of the main entrance. Figure 5
kwO	3-21-99	This sample was taken in the same location but during a different season. It had rained a little the night before. Figure 5

Figure 1: This is the stalactite that water samples kw1 and kwL were obtained from. It is hanging over rimstone dams.

Figure 2: A gypsum flower from the breakdown room. This is the room where rock sample krC was taken.

Figure 3: The main insurgence: the author is getting water sample kwA. She is kneeling on a block of fissile sandstone that has fallen from the cliff face that is to the right of her. Water sinks into the cave down and to the left of this picture.

Figure 4: These are brachiopod fossils that are found in a thin layer inside of the cave. The pencil is pointing to a cross-sectional view in which the lophophore skeleton can be seen.

Figure 5: This is the main resurgence of the cave. Local people drink the water from this spring

Table 2: Thin section descriptions.

Rock sample	Thin section description
Kr1	25% oolitic, 45% pellets, 20% well-crystallized calcite crystals, 10% shell fragments, edges of oolites and shell fragments show micritilization, matrix is sparry, well-crystallized calcite Figure 6
Kr3	60% pellets, 20% oolitic, micritic pellets, calcite crystals are well crystallized, some quartz is present. Fragments show micritilization Figure 7
Kr4	Well-crystallized corral, has large quartz crystals, some calcite twinning is present Figure 8
Kr5	20% oolitic, 75% micritic pellets, <5% quartz grains, <<5% sparry calcite, few shell fragments Figure 9
Kr6	Dolomite has very small rhobohedric crystals, micritilized calcite crystals are present, <<5% quartz crystals Figure 10
Krss	5-10% irresolvables, mostly quartz, some feldspar twinning, mostly rounded quartz Figure 11
G	These thin sections consist of small, well-aligned calcite crystals and gypsum crystals that are perpendicular to the growth rings. Figure 13

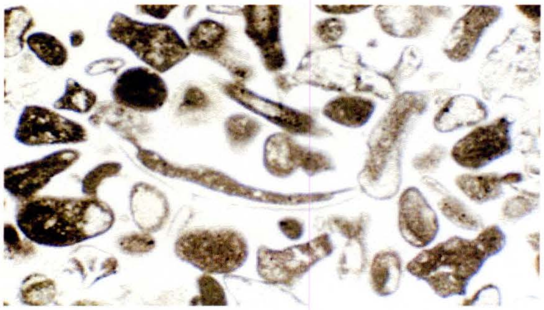
Figure 6: Thin section of kr1. The width of each figure at 40X magnification corresponds to about 2.5 mm.

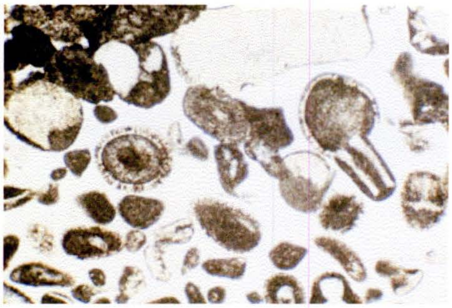
Figure 7: Thin section of kr3 . 40X magnification

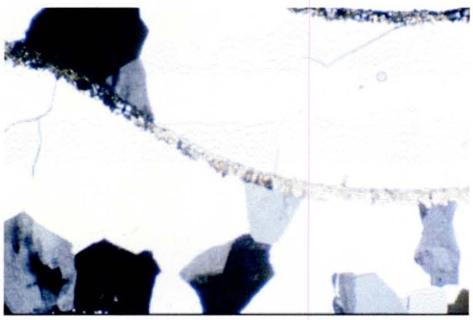
Figure 8: Thin section of kr4. 40X magnification under crossed polars

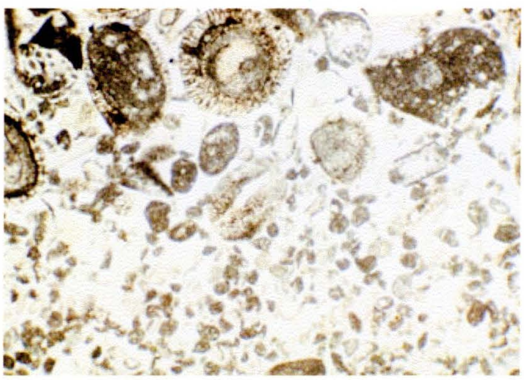
Figure 9: Thin section of kr5. 40X magnification

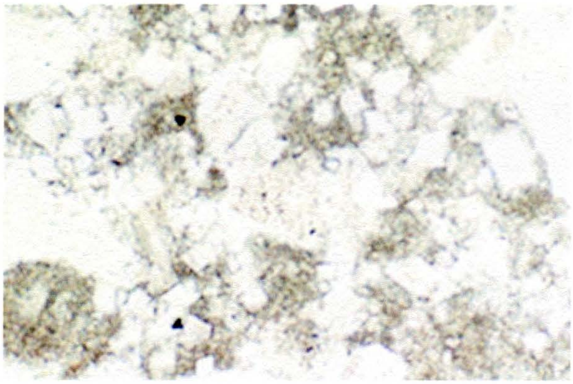

Figure 10: Thin section of kr6. The width of each figure at 100X magnification corresponds to about 1.0 mm.

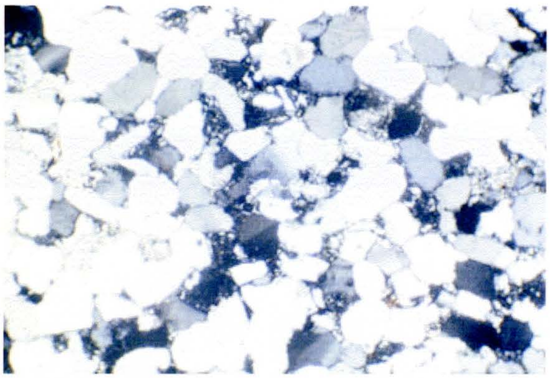

Figure 11: Thin section of sandstone. 40X magnification under crossed polars

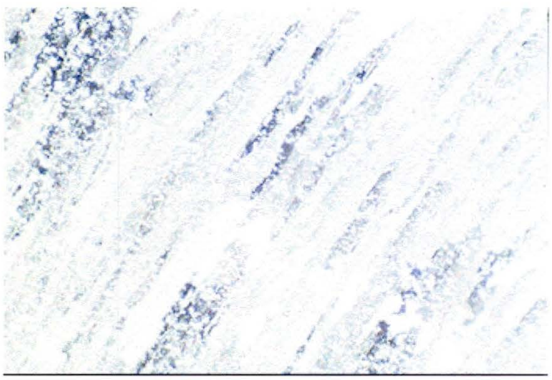

Figure 12: Thin section of stalatite sample. 100X magnification under crossed polars

IV. Results

Water samples

The Sr concentrations and $^{87}Sr/^{86}Sr$ ratios of water samples are given in Table 3. The ratios are also plotted in green on the cave map in Plate 4. The Sr concentrations vary widely, ranging from 0.018 to 0.16 ppm with an outlier at 2.65 ppm for a sample of water dripping from a stalactite. The $^{87}Sr/^{86}Sr$ ratios of the water samples range from 0.7131 at the main insurgence to 0.7084 dripping off the speleothems. Values in the main stream are between these two ratios, approximately 0.7099. Water in the main stream drops from 0.7099 to 0.7098 going downstream. The $^{87}Sr/^{86}Sr$ values are lower at the resurgence: 0.7093 in the dry season and 0.7092 at the beginning of the wet season.

Inside the cave, water samples were taken at the same locations in the dry season and at the beginning of the wet season. The $^{87}Sr/^{86}Sr$ ratios from samples taken at the beginning of the wet season were higher than those from the dry season. The difference in waters from speleothems ranged from 0.00092 from the speleothems 120 feet downstream of the east passage intersection to 0.00004 from the stalactite in the main passage. Values for samples taken from the main stream differed by 0.00035. This is close to the difference in ratios from the waterfall, which was 0.00036.

Bedrock samples

The Sr concentrations and $^{87}Sr/^{86}Sr$ ratios of rock samples are given in Table 4. The ratios are also shown in Plates 3 and 4. Overall, the rock samples vary from 0.70784 to 0.7379 with the sandstones being much higher (0.7177 to 0.7379) than the carbonates (0.70784 to 0.70827). The Sr concentrations vary from 13 ppm to 1290 ppm with the sandstones being much lower (13 to 40 ppm) than the carbonates (520 to 1290 ppm).

The rock samples krD and krE are from the Bangor Limestone just over the main insurgence. The $^{87}Sr/^{86}Sr$ ratios from these rocks are very similar close, 0.70821 and 0.70806. These rocks were about twenty feet apart from each other in the cliff-face.

The sample taken from the interbedded sandstone of the Hartselle Formation was broken into two pieces to see if there was variation in the sandstone. These $^{87}Sr/^{86}Sr$ ratios were both high, 0.7379 and 0.7337, and did show some variation. The sandstone sample from the cap of the hill, the Lee Formation, also had a high ratio of 0.7177.

The rest of the rock samples were from the Kidder and Ste. Genevieve Limestones. They are all fairly similar in $^{87}Sr/^{86}Sr$ ratios except kr6, which is a dolostone from the Kidder Limestone. The $^{87}Sr/^{86}Sr$ ratio for this sample is 0.70827 which is very close to the samples from the diffuse-flow karst waters. The Ste. Genevieve samples gave the lowest $^{87}Sr/^{86}Sr$ ratios and the least dispersion; they range from 0.70789 to 0.70784. The Kidder Limestone samples are on average a little higher in $^{87}Sr/^{86}Sr$ and also show more variation; the ratios range from 0.70789, similar to the ratios in the Ste. Genevieve Limestone, to 0.70809.

Stalactite sample

The stalactite sample is shown in Plate 5. This plate also shows where the samples were taken from in the stalactite. The Sr results are given in Table 5. The $^{86}Sr/^{87}Sr$ ratios of small samples taken from various areas of the stalactite show only minor variations. The $^{87}Sr/^{86}Sr$ ratios range from 0.708365 to 0.708427, with 0.708390 being the most common value. The water sample taken from this stalactite has a ratio of 0.708366 (12). This value is about equal to the lowest value from the stalactite itself.

Table 3: Analytical data for water samples.

Sample name	date sample was obtained	sample location	Sr ppm	$^{87}Sr/^{86}Sr$
kwA	3-21-99	main insurgence	0.0178	0.713069 (15)
kw3	11-27-98	side insurgence	0.0294	0.711029 (19)
kw4	11-27-98	Resurgence	0.0729	0.709316 (28)
kwO	3-21-99	"	0.0720	0.709212 (19)
kw7	9-5-98	water from the waterfall	0.2209	0.709028 (15)
kwJ	3-20-99	"	0.1441	0.709383 (10)
kw8	9-5-98	water from the main stream	0.1591	0.709564 (17)
kwK	3-20-99	"	0.0522	0.709912 (10)
kwE	3-20-99	water from the main stream where it flows into the cave	0.1141	0.709777 (10)
kw2	11-27-98	water from the stalactite sample	2.654	0.708366 (12)
kw5	9-5-98	Speleothems 120 feet downstream of the east intersection	0.1329	0.708605 (15)
kwH	3-20-99	"	0.1130	0.709520 (154)
kw6	9-5-98	stalactite in main passage	0.1474	0.708423 (10)
kwD	3-20-99	"	0.1308	0.708462 (15)
kw1	11-30-98	stalactite between the two entrances	0.1220	0.708370 (20)
kwL	3-20-99	"	0.1209	0.708431 (21)

The uncertainties in concentration of Sr are assigned at ± 0.1%. This uncertainty does not take into account and sample heterogeneity.

The $^{86}Sr/^{87}Sr$ ratios are normalized assuming normal Sr with $^{86}Sr/^{88}Sr = 0.119400$. The uncertainties refer to the last digit(s) and are two standard deviations of the mean in-run uncertainties. Reference value of $^{86}Sr/^{88}Sr$ for the SRM987 is 0.710242 ± 0.000010 (one-sigma external reproducibility).

Table 4: Sr analytical data for rock samples.

Sample name	date sample was obtained	sample location	Sr ppm	$^{87}Sr/^{86}Sr$
krss	1-2-99	Sandstone caprock	13.33	0.717709 (34)
krF1	3-21-99	fissile sandstone from main insurgence	28.08	0.737856 (167)
krF2	3-21-99	"	38.97	0.733747 (21)
krD	3-21-99	limestone from main insurgence	519.5	0.708209 (16)
krE	3-21-99	"	653.1	0.708063 (10)
kr6	11-27-98	dolostone from west passage	1291	0.708272 (25)
krC1	3-20-99	limestone from breakdown room	698.6	0.707976 (7)
krC2	3-20-99	"	945.5	0.707929 (8)
krA	3-20-99	limestone from ceiling of canyon to waterfall	278.7	0.708093 (7)
krB	3-20-99	oolitic limestone from that canyon wall	672.8	0.707944 (8)
kr1-rs	9-5-98	limestone from canyon leading to west passages	1041	0.707892 (12)
kr1-s	9-5-98	"	1043	0.707938 (15)
kr3	9-5-98	limestone from main stream passage	669.3	0.707893 (12)
kr5	9-5-98	banded limestone from bottom of sand hill	786.1	0.707841 (9)

The uncertainties in concentration of Sr are assigned at ± 0.1%. This uncertainty does not take into account and sample heterogeneity.

The $^{87}Sr/^{86}Sr$ ratios are normalized assuming normal Sr with $^{86}Sr/^{88}Sr = 0.119400$. Uncertainties refer to the last digit(s) and are two standard deviations of the mean in-run uncertainties. Reference value of $^{86}Sr/^{88}Sr$ for the SRM987 is 0.710242 ± 0.000010 (one-sigma external reproducibility).

Table 5: Sr analytical date for samples of the stalactite sample. Plate 5 shows the stalactite sample and where the samples were taken from.

Sample name	date sample was obtained	sample location	ppm	$^{87}Sr/^{86}Sr$
gl	11-27-98	formation's outer layer	9797	0.708396 (13)
g2a	11-27-98	next layer in	4251	0.708386 (8)
g2b	11-27-98	"	4068	0.708390 (17)
g2c	11-27-98	Next layer in	4004	0.708397 (18)
g3a	11-27-98	"	3420	0.708379 (9)
g3b	11-27-98	"	1001.1	0.708365 (7)
g4a	11-27-98	center of formation	4795	0.708385 (15)
g4b	11-27-98	"	709.7	0.708427 (15)

The uncertainties in concentration of Sr are assigned at ± 0.1%. This uncertainty does not take into account and sample heterogeneity.

The $^{87}Sr/^{86}Sr$ ratios are normalized assuming normal Sr with $^{86}Sr/^{88}Sr = 0.119400$. Uncertainties refer to the last digit(s) and are two standard deviations of the mean in-run uncertainties. Reference value of $^{86}Sr/^{88}Sr$ for the SRM987 is 0.710242 ± 0.000010 (one-sigma external reproducibility).

V. Discussion

The main sources of Sr for the water and the cave deposits associated with the Redmond Creek Cave are the bedrocks of the area through which the ground and stream water flow. The $^{86}Sr/^{87}Sr$ ratios for the two main types of bedrock, sandstone and limestone are very different. The differences are substantial and important. The values found for the sandstone (~0.734) and for the limestone (~0.7080) are very reasonable values for these bedrocks.

Both bedrock types show Sr heterogeneities that are also reasonable. The high $^{86}Sr/^{87}Sr$ ratios for the sandstones can be interpreted to indicate either that the detrital components had elevated $^{86}Sr/^{87}Sr$ ratios at the time of deposition or that these rocks have an elevated Rb/Sr ratios that have increased the $^{86}Sr/^{87}Sr$ ratios due to the production of *in situ* ^{87}Sr by ^{87}Rb decay since deposition or both. This may be determined by measuring the sandstone Rb concentrations but this was not attempted in the present study. The actual cause is not very important to the interpretation for which the present sandstone $^{86}Sr/^{87}Sr$ ratios are important.

In contrast to the sandstones, the limestones show much lower $^{86}Sr/^{87}Sr$ ratios and less variation. The limestone values for $^{86}Sr/^{87}Sr$ are similar to those of Paleozoic seawater which is to be expected for these marine deposits. The Rb was not measured in the limestones but the Rb/Sr can be assumed to be so low that the $^{86}Sr/^{87}Sr$ ratio did not change over time due to ^{87}Rb decay. The $^{86}Sr/^{87}Sr$ ratios of the limestones may be affected by diagenesis or the incorporation of detrital material. These processes may explain the small variations that are observed. One sample carbonate bedrock, kr6, is dolomitic and does show some alteration and has an elevated ratio that is likely due to diagenetic effects.

The limestone $^{86}Sr/^{87}Sr$ ratios may be compared to the values reported for Paleozoic seawater, which vary over geologic time. The values for the Ste. Geneviere Limestone are about 0.70785. On the Sr seawater curve constructed by Denison et al. (1994) this value is seen at the Chesterian Stage which falls at an age of about 325 million years. Thus, the $^{86}Sr/^{87}Sr$ ratios of the limestones indicate a Mississippian age that agrees very well with the stratigraphical and paleontological indicators.

The water in the Redmond Creek area passes through the both sandstone and carbonate bedrock. Therefore, the Sr in waters can be considered a mixture of that derived from each bedrock. Significantly, all water samples give $^{86}Sr/^{87}Sr$ ratios that are between those for the carbonate and sandstone bedrock. The differences in $^{86}Sr/^{87}Sr$ ratios among waters can be regarded to indicate different amounts of Sr from the two rock types.

By assuming that the water Sr is a mixture of that from two components, the fractions each component may be estimated. The two endmembers can be approximated for $^{86}Sr/^{87}Sr$ as: 0.7079 for carbonate and 0.734 for sandstone. These values are approximations but variations of the scope seen in the present study will have only small effects on the calculated fractions. For each water sample, the fraction of strontium (f_{ss}) from the sandstone in samples was calculated using the formula:

$$f_{ss} = [(^{87}Sr/^{86}Sr)_{sample} - (^{87}Sr/^{86}Sr)_{carbonate}] \,/\, [(^{87}Sr/^{86}Sr)_{sandstone} - (^{87}Sr/^{86}Sr)_{carbonate}]$$

The results of the calculation are given in Table 6. The components range from about 25 to 20% of the Sr from sandstone. That the limestone predominates contributing from 80 to 98% of the Sr in the waters can be interpreted to reflect both the much higher Sr concentration of Sr in the limestones and the more readily that the limestone reacts or dissolves. Notably, the fraction of the Sr derived from the sandstone decreases with increased distance from the point where waters will have traversed the sandstone bedrock. The lowest $^{86}Sr/^{87}Sr$ ratios and the smallest sandstone fractions are seen for water that drips from the speleothems. Also, the ratios are higher for waters that are flowing in conduits. Thus, the results support the indication that more bedrock interaction occurs with slow and diffuse flow through the carbonates compared to channel flow.

Where sampled at different times, the waters from all but one location show higher $^{86}Sr/^{87}Sr$ ratios for the wet season. This is likely due to the increase in water) and flow rate) that has passed through the sandstone above the cave, providing less time to interact with the carbonate. The only sample that showed a decrease in isotopic ratio in the wet season was the sample taken from the cave's resurgence. This decease may be due to the increased distance between the resurgence and the sandstone source of the higher $^{86}Sr/^{87}Sr$ ratios.

A difference can be seen in the ratios for the diffuse flow water and the conduit flow water in the main stream passage. The diffuse flow water is the water that was obtained from dripping speleothems. The main stream has a fraction of Sr from the sandstone that is more than three times the fraction present in the diffuse flow waters.

The stalactite $^{86}Sr/^{87}Sr$ ratios show very limited dispersion. The values are similar or identical for individual growth zones. This contrasts with the seasonal variations seen for the conduit-flow samples. The $^{86}Sr/^{87}Sr$ ratios are not uniform in the stalactite but the variations, relatively, are much, much less. This must reflect a long term averaging that takes place with diffuse water flow that produces the speleothems.

Similar sectioning and Sr analysis was preformed on a Tasmanian speleothem by Geode et al. (1998). These authors found significant long-term $^{86}Sr/^{87}Sr$ variations which they attributed to Paleozoic dusts being blown into the cave. In contrast, the uniform $^{86}Sr/^{87}Sr$ ratios from the stalactite of Redmond Creek Cave suggest a stable environment over the time of deposition. The uniformity of $^{87}Sr/^{86}Sr$ ratios in the Redmond Creek Cave stalactite suggests that the paths of water flow for this speleothem did not change appreciably over the time of its deposition.

Table 6: Calculated fraction of Sr from the sandstone in each water sample.

Sample name	date sample was obtained	sample location	Fraction of sandstone Sr
kwA	3-21-99	main insurgence	0.20
kw3	11-27-98	side insurgence	0.12
kw4	11-27-98	Resurgence	0.054
kwO	3-21-99	"	0.050
kw7	9-5-98	water from the waterfall	0.043
kwJ	3-20-99	"	0.057
kw8	9-5-98	water from the main stream	0.064
kwK	3-20-99	"	0.077
kwE	3-20-99	water from the main stream where it flows into the cave	0.072
kw2	11-27-98	water from the formation sample	0.018
kw5	9-5-98	formations 120 feet downstream of the east intersection	0.027
kw6	9-5-98	stalactite in main passage	0.020
kwD	3-20-99	"	0.022
kw1	11-30-98	formation between the two entrances	0.018
kwL	3-20-99	"	0.020

A fraction of $^{87}Sr/^{86}Sr$ from the sandstone (f_{ss}) present was calculated for each water sample using the equation:

$$f_{ss} = [(^{87}Sr/^{86}Sr)_{sample} - (^{87}Sr/^{86}Sr)_{carbonate}] \,/\, [(^{87}Sr/^{86}Sr)_{sandstone} - (^{87}Sr/^{86}Sr)_{carbonate}]$$

The endmember values used are 0.7079 for carbonate and 0.734 for sandstone.

VI. Conclusions

1. The strontium in the water samples associated with the Redmond Creek Case system derive from the sandstone and carbonate bedrock, where the latter rock type predominates. The estimates are that from 2 to 20% of the Sr in the waters come from the sandstone bedrock.

2. There is a significant difference in the $^{87}Sr/^{86}Sr$ ratios of the conduit flow waters and the diffuse flow waters. These are attributed to the interaction of water with bedrock.

3. The limestone bedrock is about 325 million years old based up the limestone $^{87}Sr/^{86}Sr$ ratio and published seawater $^{87}Sr/^{86}Sr$ curves.

4. The sources for the Sr have not changed significantly in the recently formed stalactite appear to be constant over the period of formation.

VIII. References

Choquette, Phillip W. and Randolph P. Steinen (1980) Mississippian non-supratidal dolomite, Ste. Genevieve Limestone, Illinois Basin: evidence for mixed water dolomitization in *Concepts and models of dolomitization* ed. Donald H. Zenger, John B. Dunham, and Raymond L. Ethington, Society of Economic Paleontologists and Mineralogists p. 163-177.

Denison, R. E., R. B. Koepnik, W. H. Burke, E. A. Hetherington, and A. Fletcher (1994) Construction of the Mississippian, Pennsylvanian and Permian seawater 87Sr/86Sr curve, *Chemical Geology*, 112: 145-167.

Dickin, Alan P. (1995) *Radiogenic Isotope Geology* Cambridge University Press, New York.

Foland, K. A. and J. C. Allen (1991) Magma sources for Mesozoic inorganic granites and of the White Mountain magma series, New England, USA, *Contributions to Mineralogy and Petrology* 109: 195-211.

Faure, Gunner (1986) *Principles of Isotope Geology* second edition John Wiley & Sons, New York.

Geode, Albert, Malcolm McColloch, Frank McDermontt, and Chris Hawkesworth (1998) Aeolian contribution to strontium and strontium isotopic variations in a Tasmanian speleothem, *Chemical Geology* 149: 37-50.

Hess, John W., Stephen G. Wells, James F. Quinlan, and William B. White. (1989) Hydrogeology of the south-central Kentucky karst in *Karst Hydrology: concepts from the Mammoth Cave area,* ed. by White, William B. and Elizabeth L. White. Van Nostrand Reinhold, New York.

Hess, John W. and William B. White (1989) Chemical Hydrology in *Karst Hydrology: concepts from the Mammoth Cave area,* ed. by White, William B. and Elizabeth L. White. Van Nostrand Reinhold, New York.

Hill, Carol and Paolo Forti (1997) Cave minerals of the world National Speleological Society, Alabama.

Lewis, Richard Q. Jr. (1977) Geologic map of the Powersburg Quadrangle and part of the Pall Mall Quadrangle, Wayne and Clinton Counties, Kentucky. GQ-1377 USGS.

John MacGregor (1985) Identification charts of bats, Kentucky Department of Fish and Wildlife, Frankfort Kentucky

Moore, George W. and G. Nicholas Sullivan. (1964) *Speleology: the study of caves,* Zephrus Press Inc, New Jersey.

Rice, Charles L., Edward G. Sable, Garland R. Dever, Jr.,